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PIEZOELECTRICITY IN GAMMA-FORM NYLON 11.(U)

AUG 81 J I SCHEINBEIM, B A NEWMAN

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1. REPORT NUMBER Technical Report #1	2. GOVT ACCESSION NO. AD-A102823	3. RECIPIENT'S CATALOG NUMBER 823
4. TITLE (and Subtitle) Piezoelectricity in γ -Form Nylon 11	5. TYPE OF REPORT & PERIOD COVERED Technical FTJ	
7. AUTHOR(s) J. I./Scheinbeim and B. A. Newman		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept. of Mechanics and Materials Science College of Engineering, Rutgers University P.O. Box 909, Piscataway, NJ 08854		8. CONTRACT OR GRANT NUMBER(s) N00014-80-C-0795
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 11 1011 1 11
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 11 11 1-1		12. REPORT DATE August 1, 1981
LEVEL		13. NUMBER OF PAGES
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Nylon 11, piezoelectricity, temperature dependence, gamma crystal form		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) X-ray studies of unpoled and poled γ -form Nylon 11 films indicate that the polarization mechanism is not due to a field induced crystal transformation from the γ to the α form, suggesting the existence of a polar γ form. The temperature dependence of d_{31} shows no decrease in polarization at the α - γ transition temperature ($\sim 95^\circ\text{C}$) indicating that the hydrogen bonds in the poled film are not able to randomize. These results suggest the possibility that our understanding of the γ form structure of Nylon 11 is incomplete.		

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Contract N00014-80-C-0795

Technical Report No. 1

PIEZOELECTRICITY IN γ -FORM NYLON 11

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J. I. Scheinbeim and B. A. Newman

Prepared for Publication

in the

Journal of Applied Physics

Rutgers University
College of Engineering
Department of Mechanics and Materials Science
Piscataway, NJ

August 1, 1981

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PIEZOELECTRICITY IN γ -FORM NYLON 11

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Abstract

X-ray studies of unpoled and poled γ -form Nylon 11 films indicate that the polarization mechanism is not due to a field induced crystal transformation from the γ to the α form, suggesting the existence of a polar γ form. The temperature dependence of d_{31} shows no decrease in polarization at the α - γ transition temperature ($\sim 95^\circ\text{C}$) indicating that the hydrogen bonds in the poled film are not able to randomize. These results suggest the possibility that our understanding of the γ form structure of Nylon 11 is incomplete.

Introduction

Recent investigations in our laboratory of the piezoelectric activity of poled Nylon 11 films¹ raise some interesting questions about the nature of one of the two known polymorphic crystal forms - the γ form. These investigations showed that the poling of films containing the γ crystal form resulted in significantly higher piezoelectric activity than the poling of films containing the α form under identical poling conditions. The lower activity found for the α form films are consistent with the earlier studies of Kawai and Heiji^{2,3} and Litt, Hsu and Basu.⁴

In our previous study,¹ we assumed that the polar α form, consisting of hydrogen bonded sheets,⁵ would be more difficult to pole than the nonpolar γ form, in which the hydrogen bonds are randomly distributed in directions

perpendicular to the chain axis.⁶ The results obtained supported our assumption. We also assumed that poling of the γ form would result in an electric field induced phase transition from the disordered hydrogen bonding of the γ form to the ordered α form with a resultant preferential alignment of hydrogen bond dipoles (α form crystallites) in the field direction. Preliminary x-ray diffraction studies⁷ of unpoled and poled γ form films indicated that this might be the case; however, the observed x-ray changes produced by poling were quite small.

With our assumptions about the higher piezoelectric activity of γ form films verified, and with our knowledge of the crystal structures of the polar α form⁵ and the nonpolar γ form⁶ and, in addition, with the knowledge that the α form undergoes a gradual transition to the γ form with increasing temperature, as in the case for other Nylons,⁶ we assumed that Nylon 11 would have a Curie temperature of -95°C where only the disordered hydrogen bonding arrangement of the γ form exists. To verify this last assumption, we measured the temperature dependence of the piezoelectric strain coefficient, d_{31} , of a poled initially γ form film, expecting it to go to zero at 95°C when the field oriented polar α crystallites converted to the nonpolar γ form. The results reported in this work contradict this assumption and, in fact, indicate that that the γ form can also be polar.

Nylon 11 Crystal Structures

α Form: The crystal structure of the α form of Nylon 11, suggested by Slichter⁵ and modified by Newman et al,⁶ consists of hydrogen bonded sheets, with the hydrogen bonds in the plane formed by the a and c crystallographic axes of the triclinic unit cell: c is the chain direction and the hydrogen

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bonds are perpendicular to \underline{c} . The hydrogen bonding arrangement is shown in Fig. 1. All the N-H...O hydrogen bonds point in the same direction and the structure is polar.

γ Form: On the basis of their observation that the thermal expansion of Nylon 11 in the γ form ($T > 95^\circ\text{C}$) is isotropic about the chain direction, Newman et al⁶ proposed a pseudohexagonal lattice for the γ structure, with the hydrogen bonds distributed isotropically (randomly) in directions perpendicular to the chain axis. A projection of this pseudohexagonal cell and its relationship to the triclinic unit cell is shown in Fig. 2. If one assumes that the chain at the center of the pseudohexagonal cell randomly forms hydrogen bonds with any of its six neighbors, the thermal expansion of the γ form will be isotropic as has been previously reported.⁶ The resulting structure is nonpolar and the hydrogen bonds are assumed to be able to break and reform.⁶

Experimental

Unoriented, three mil (75 micron) thick films of α form Nylon 11 were heated in a vacuum oven to the melt and then quenched in liquid nitrogen. This procedure freezes in the disordered γ structure which is then stable at room temperature. The films were then poled under vacuum ($\sim 10^{-5}$ torr) at 85°C for thirty minutes at 300 KV/cm and cooled under field to room temperature. The temperature dependence of the piezoelectric strain coefficient, d_{31} , was then determined using a Toyo Seiki Piezotron. Transmission x-ray diffraction studies were performed using $\text{CuK}\alpha$ radiation and the diffraction patterns were recorded on film.

Results and Discussion

To confirm the existence of a Curie temperature at -95°C , we measured the temperature dependence of the piezoelectric strain coefficient d_{31} which is shown in Fig. 3. d_{31} increases slowly with increasing temperature until the neighborhood of the glass transition is reached ($T_g \approx 60^{\circ}\text{C}$) and then begins to increase rapidly with increasing temperature. The expected decrease in piezoelectric response at the crystal transition temperature is not observed. Instead, d_{31} continues to increase rapidly with increasing temperature to a value of ~ 12 PC/N at the maximum measurement temperature of 107°C . Since the piezoelectric strain constant, d_{31} , is a measure of the change in film polarization normal to the film surface with applied stress in the plane of the film ($d_{31} \equiv \frac{1}{A} \frac{dP_1}{d\sigma_{31}}$, where A is the electrode area and σ_{31} is the stress in the plane of the film) it is obvious that the film polarization does not go to zero at the α to γ crystal phase transition temperature. In fact, it appears that the transition has no significant effect on film polarization.

The implications of these results are quite clear. First, since the film is γ form before poling (See Fig. 4) and primarily γ form after poling (See Fig. 5), the quenched γ form is somehow able to rearrange its hydrogen bonding configuration to produce a net polarization, i.e., the electric dipoles formed by the $\text{N-H}\dots\text{O}=\text{C}$ hydrogen bonds are preferentially aligned in the field direction. Second, at and above the transition temperature, the hydrogen bonds in the poled sample are not able to randomize and freely rearrange their direction as proposed by Newman et al.,⁶ since there is no indication of any decrease in film polarization (as indicated by the continuing rapid increase in d_{31}) in this temperature region.

To account for the fact that the γ form crystals can be made to exhibit a net polarization while still exhibiting isotropic thermal expansion perpendicular

to the chain direction, we propose the following model: First, the basic γ form structure suggested by Newman et al⁶ for Nylon 11 is assumed to be correct. This means that the hydrogen bonds on any given chain can point towards any of the six neighboring chains as shown in Fig. 4a. This figure may also be viewed as a projection down the chain axis of the random hydrogen bonding directions about the center chain (or any chain), for both the γ structure which has been frozen in by quenching and the γ structure which exists above 95°C. This structure is nonpolar and has isotropic thermal expansion about the chain direction as indicated by the single x-ray diffraction ring corresponding to both the (100) and (010) reflections as shown in Fig. 4b. In order to preferentially align the dipoles in the field direction during poling, the hydrogen bonds must switch - i.e., the hydrogen bonds must break and reform. However, the poled γ structure must still exhibit isotropic thermal expansion about the chain direction, since the single γ form (100) (010) x-ray diffraction ring is still observed for the poled film as shown in Fig. 5b. These conditions would be satisfied if the initially disordered dipole arrangement of the quenched γ form converted to the preferentially aligned dipole arrangement shown in Fig. 5a. The thermal expansion of this polarized γ structure would still be isotropic about the chain direction.

The proposed model for obtaining a polar γ structure is based on the switching by multiples of 60° as has been proposed by Kepler and Anderson⁸ for poly(vinylidene fluoride).

Another mechanism of electric field induced dipole reorientation is possible for Nylon 11 which is, of course, unavailable for poly(vinylidene fluoride); the switching of the amide hydrogen from the nitrogen to the oxygen which would change the N-H...O hydrogen bond to an N ... H-O hydrogen bond producing a change in the dipole direction. This polarization mechanism appears less likely to occur than the first mechanism proposed for several

reasons, one of which is that it is also available as a switching mechanism for the α structure which does not pole as well as the γ structure. However, without additional studies this mechanism must still be considered possible and will be investigated in future infrared studies.

The concept of a polar γ form for Nylon 11, although consistent with our piezoelectric and x-ray data, creates some difficulties. If the Newman et al⁶ assumption of a randomization of the hydrogen bonding occurring above the α to γ transition temperature is correct, why doesn't the piezoelectric response of the poled γ structure go to zero above 95°C where the hydrogen bonds are presumably free to break and reform? This may be explained if the proposed randomization of hydrogen bonds in the γ form structure is incorrect. It should be pointed out that a complete x-ray crystal structure determination has not been done for Nylon 11 in either the α or γ forms.

One obvious reason for questioning the proposed structure of Nylon 11 is apparent in Newman's et al⁶ temperature dependent x-ray diffraction studies. The halfwidth's of the (100) and (010) reflections in the α form are $\sim 2^\circ$ in 2θ . In the γ form, the halfwidth of the combined (100) (010) reflection is $\sim 1^\circ$ in 2θ . Although this may be explained by thermally reversible changes in crystal size or perfection, other explanations may exist, including, as suggested, that one or both of the proposed structures is incorrect.

Conclusions

Examination of the x-ray diffraction patterns of unpoled and poled γ form Nylon 11 films indicates that the polarization mechanism is not a field induced phase transformation from the disordered nonpolar γ form to an oriented α form. Since the poled films exhibit the same single diffraction ring as the unpoled

films, we propose a polar γ -form. This polar γ form would also exhibit isotropic thermal expansion perpendicular to the chain direction as has been previously observed for the nonpolar γ form.⁶

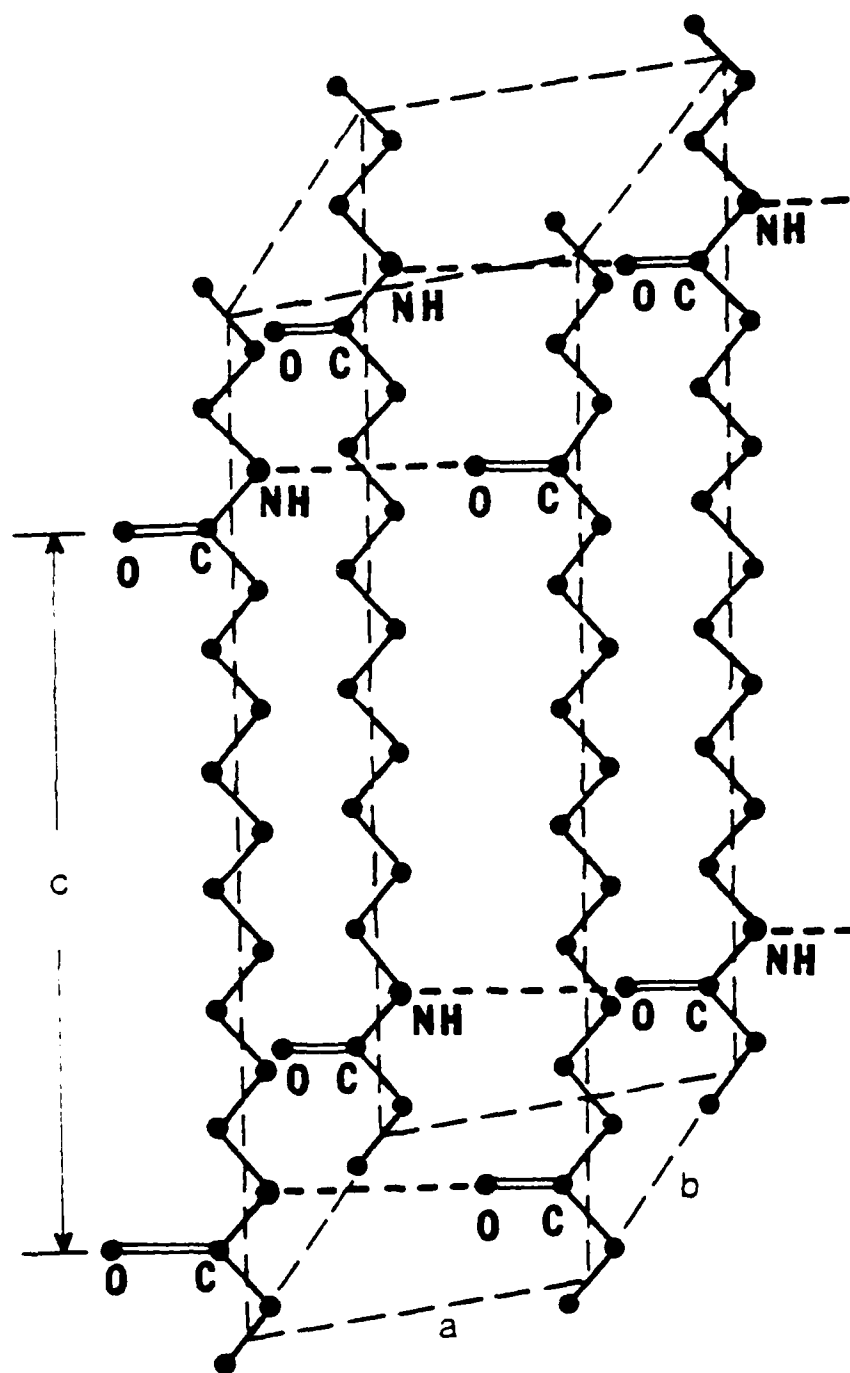
A determination of the temperature dependence of the piezoelectric strain coefficient, d_{31} , indicates that the field induced alignment of hydrogen bonds does not randomize at or above the 95°C transition temperature. This suggests the possibility that the previously proposed Nylon 11 γ form structure, based on a randomization of hydrogen bonds above 95°C, may not be correct. Future crystallographic studies of Nylon 11 will hopefully provide additional structural information.

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Figure Captions

- Figure 1: The suggested α form unit cell of nylon 11 showing the polar hydrogen bonded sheet structure.
- Figure 2: A c axis projection of the proposed triclinic (α form) and pseudohexagonal (γ form) unit cells.
- Figure 3: Temperature dependence of the piezoelectric strain coefficient d_{31} from 0°C to 107°C.
- Figure 4a: c axis projection of the pseudohexagonal γ form of nylon 11 showing the random hydrogen bonding of the center chain to its neighbors.
- Figure 4b: X-ray diffraction pattern of the γ form film.
- Figure 5a: c axis projection of the electric field oriented polar γ form of nylon 11.
- Figure 5b: X-ray diffraction pattern of the poled (polar) γ form film.



NYLON - 11

Figure 1

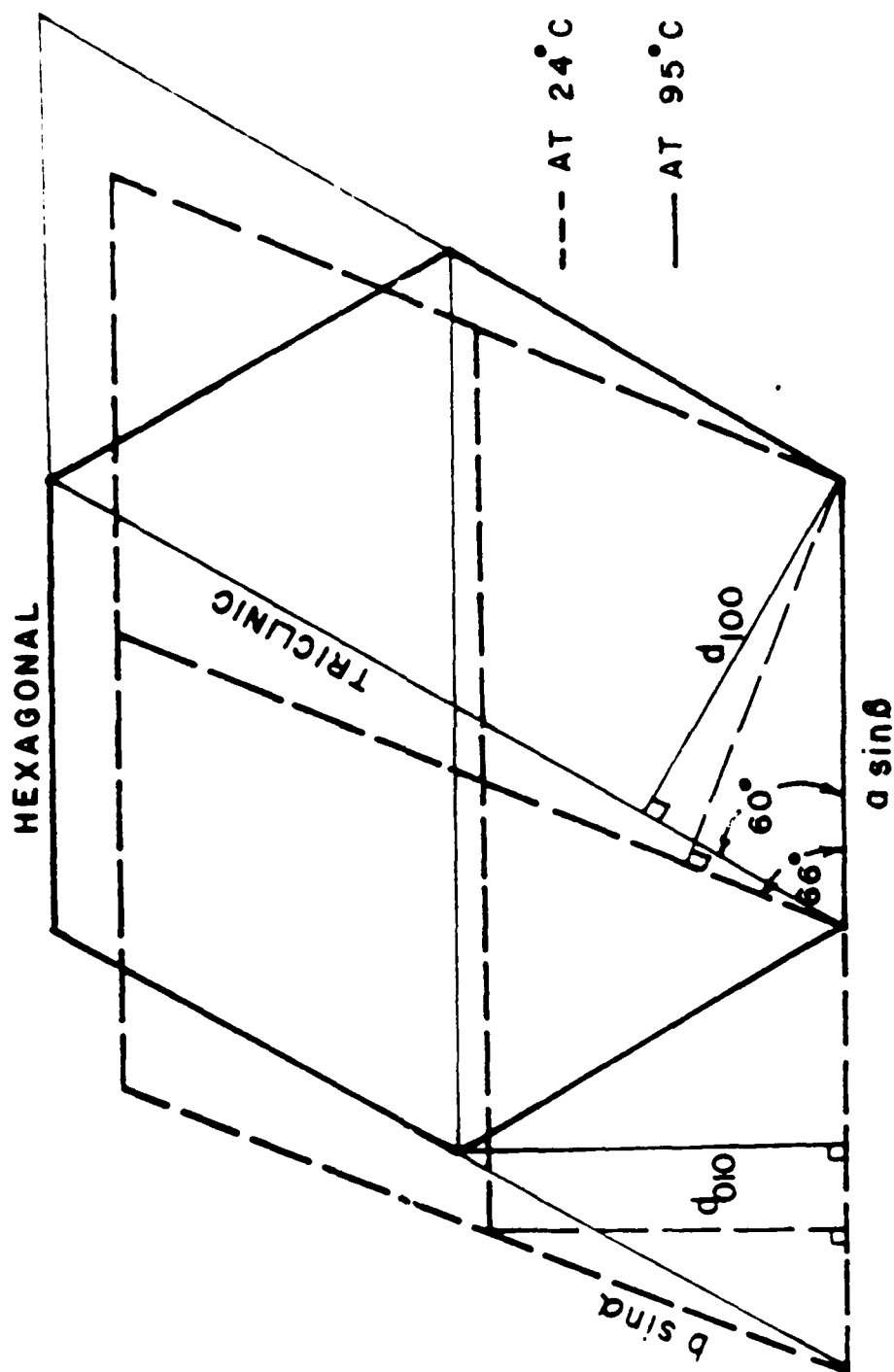


Figure 2

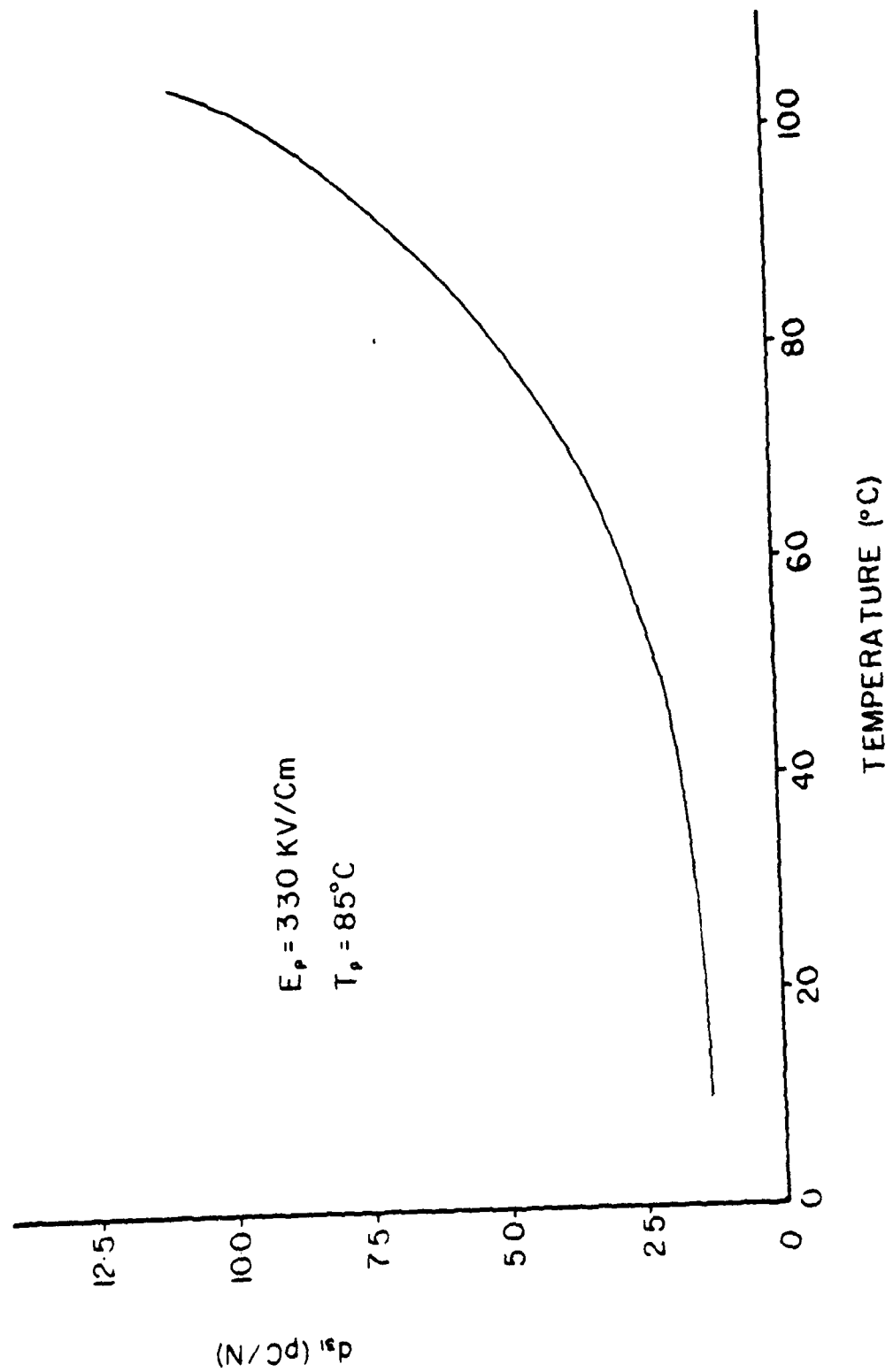


Figure 3

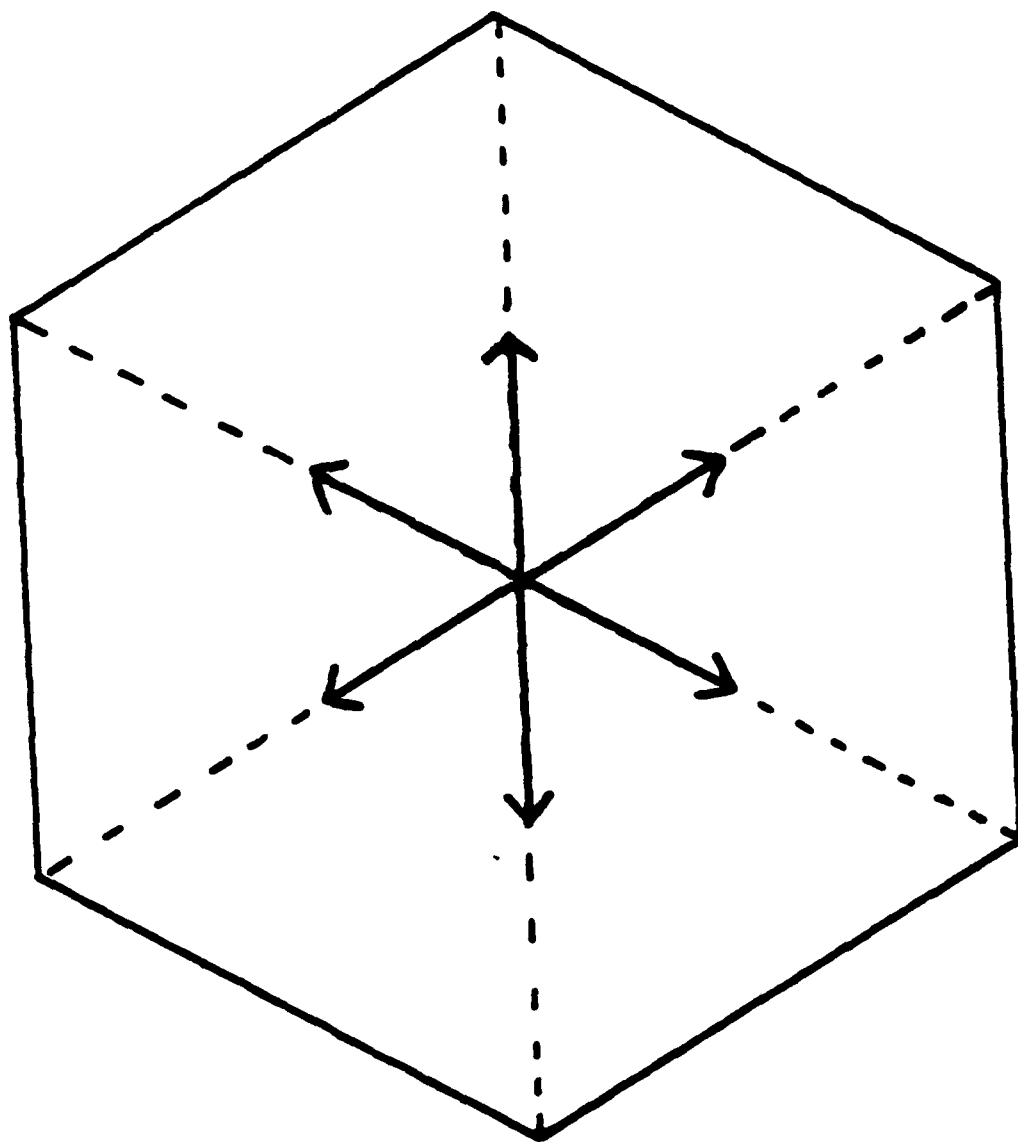


Figure 4a



Figure 4b

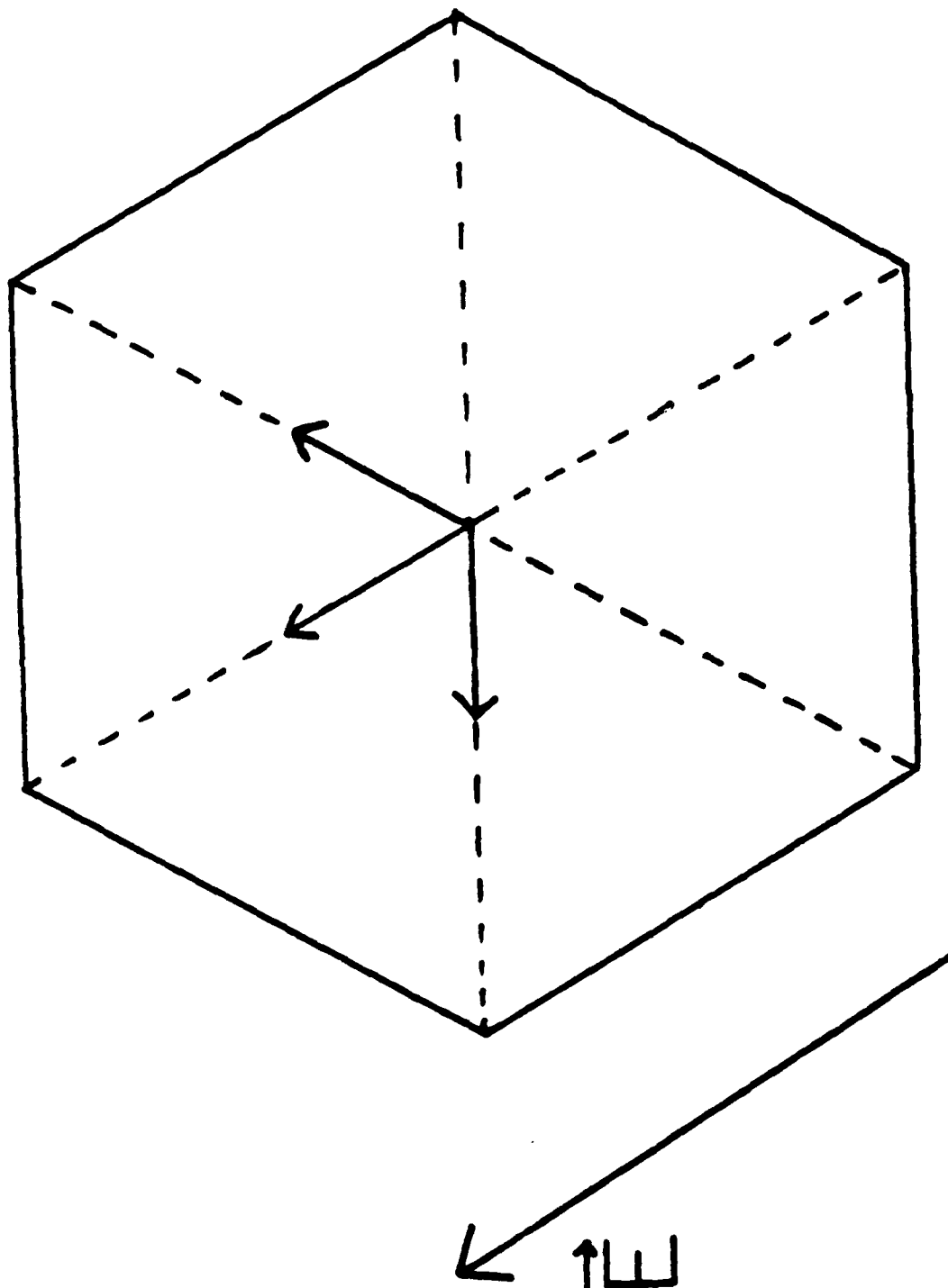


Figure 5a

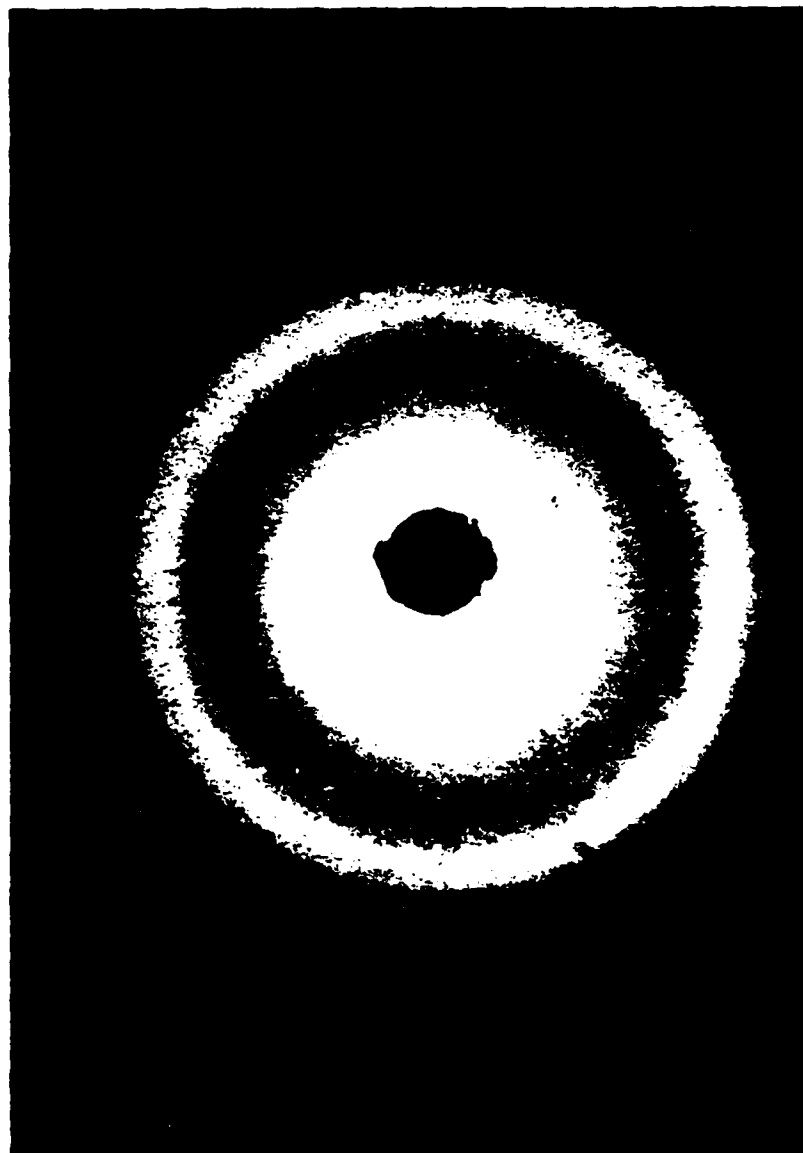


Figure 5b

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